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Analysis of Surface Hydrogen in High-Strength Steels

V.S. Sastri and D.B. McDonnell

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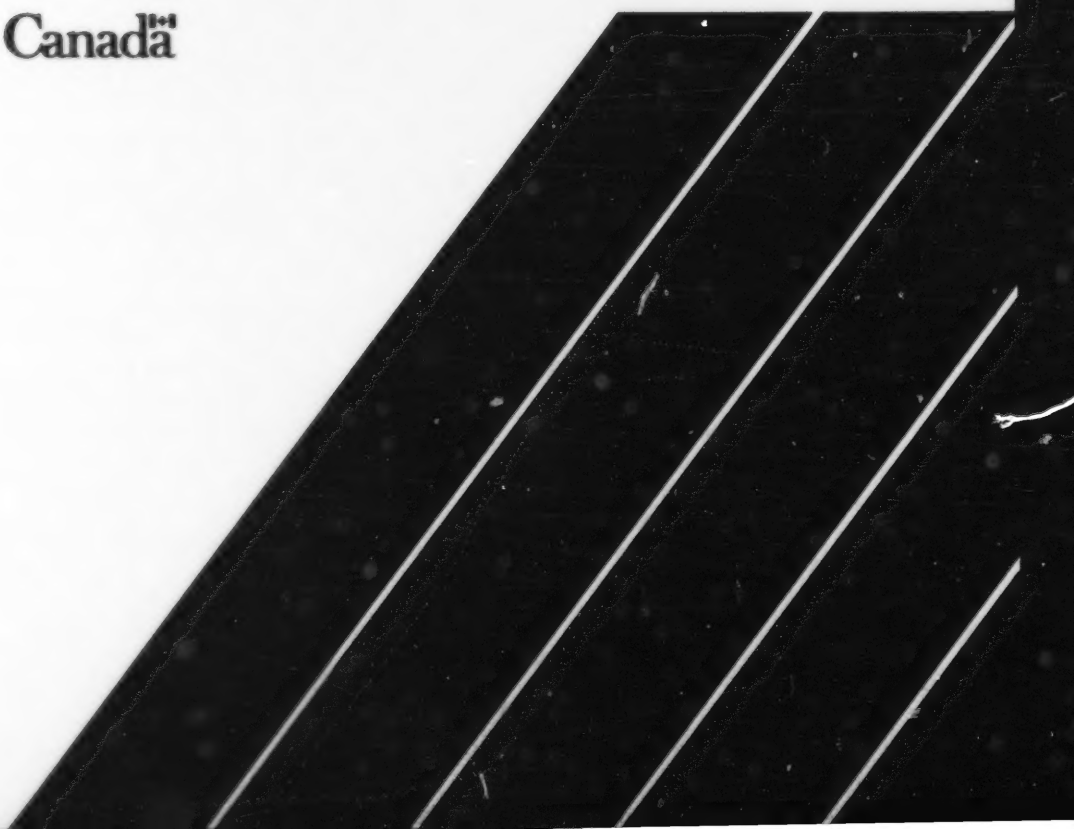

METALS TECHNOLOGY LABORATORIES

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REPORT MTL 90-6(TR)

ANALYSIS OF SURFACE HYDROGEN IN HIGH-STRENGTH STEELS

by

V.S. Sastri* and D.B. McDonnell**

ABSTRACT

Nitroxyl free radical was used in the determination of hydrogen in high-strength steels 4037 and 1062. Polarography and electron spin resonance techniques were used to determine the unreacted free radical in solution. Secondary ion mass spectrometry (SIMS) profiles showed the enrichment of the steels with deuterium in the outer surface layers.

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LABORATOIRES DE LA TECHNOLOGIE DES MÉTAUX
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DOSAGE DE L'HYDROGÈNE DANS LES COUCHES SUPERFICIELLES DES ACIERS À HAUTE RÉSISTANCE

par

V.S. Sastri* et D.B. McDonnell**

RÉSUMÉ

On a utilisé des radicaux libres nitroxyles pour doser l'hydrogène dans les aciers à haute résistance 4037 et 1062. On a fait appel à la polarographie et à la résonance paramagnétique électronique pour déterminer la quantité de radicaux libres non réagis dans la solution. L'examen des spectres de masse à émission ionique secondaire (SIMS) a révélé que les couches superficielles des aciers présentaient une teneur plus élevée en deutérium.

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INTRODUCTION

The desire to resolve the problem of hydrogen embrittlement in high-strength steels led to the development of analytical methods suitable for characterizing its transport behaviour and metallurgical effects. Methods such as vacuum extraction (1-3) and tin-fusion (4) have proven of value in assessing procedures including the nitric, acetic, phosphoric (NAP) acid treatment (5-7) which aim to reduce surface hydrogen concentrations. This paper describes the application of three additional analytical techniques: electron spin resonance (ESR), voltammetry, and secondary ion mass spectrometry (SIMS) in the investigation of bulk and surface-bound hydrogen in two high-strength steels, AISI 1062 and 4037.

VOLTAMMETRY

Although free radicals may appear to be of doubtful utility as analytical reagents, certain compounds in the family of stable nitroxyl radicals such as 2,2,6,6 tetramethyl oxypiperidine 1-oxyl (R-1 thanol) have found applications as spin labels in molecular biology and as working substances for high-sensitivity nuclear procession magnetometers (8). Klyachko et al. (9) have indicated that R-1 thanol may be used to determine hydrogen in steel indirectly, through amperometric titration of the unreacted reagent after the release of surface hydrogen by controlled current electrolysis.

ESR

Because all free radicals are paramagnetic, electron spin resonance has been used extensively in investigations of nitroxyl-free radicals including R-1 thanol (8). Herein, ESR was employed as an alternative technique to voltammetry for analysing unreacted R-1 thanol reagent after electrolysis.

SIMS

Secondary ion mass spectrometry is a surface spectroscopic technique capable of analysing all elements in the periodic table, including isotopes. Applications have included studies of the segregation of deuterium to external surfaces and grain boundaries in nickel (10) and niobium (11), of deuteride formation at crack tips in niobium (12), of the measurement of the lateral distribution of hydrogen in welded portions of carbon (13) and stainless (14) steels and of hydrogen in silica (15). Deuterium-charged steels are employed in order to minimize any hydrogen background associated with the presence of water vapour in the mass spectrometer.

EXPERIMENTAL

The commercially available pins of 1062 and 4037 steel were identical to those used previously (8). Their total hydrogen content was measured in a Leybold-Heraeus hydrogen determinator (hot extraction method) model H2A 2002 with an accuracy of ±0.1 ppm and a resolution of ±0.01 ppm. The instrument was calibrated with both standard steel balls containing 1.9 ppm hydrogen and with injections of known volumes of hydrogen gas calculated to give a response corresponding to 9.6 ppm.

VOLTAMMETRY

DC and differential pulse polarograms were recorded in order to first assess the thermal stability and redox behaviour of R-1 thanol in Britton-Robinson buffer solutions. Polarograms were obtained with a PAR 174 Polagraphic Analyser employing a saturated calomel reference electrode and a platinum-wire counter electrode. All voltage scans were made from +0.1 to -1.4 V (vs. SCE) at a sweep rate of 2 mV/s and a drop time of 2 s. The mass flow-rate of the dropping mercury electrode was 1.642 mg/s and the modulation amplitude was 50 mV in the differential pulse mode.

AISI type 4037 steel samples (0.38 cm diameter, 6.68 cm length, exposed length 2.54 cm) were electrolysed in 250 mL of Na_2SO_4 electrolyte (60 g/L) containing a 2.0×10^{-6} M solution of R-1 thanol.

ESR

Aliquots of R1 thanol taken from the electrolysis cell were analysed by ESR on a Brucker model 200 spectrometer at the following settings: time constant 0.3 s, microwave power 20 mW, modulation frequency 10^{-5} Hz, receiver gain 4×10^3, microwave frequency 9.045 Hz, and modulation amplitude 16.

SIMS

Secondary ion mass spectrometric measurements were made in a Cameca IMS-3F ion microscope using a primary beam of Cs^+ (500-1200 nA current and 10 keV accelerating voltage). Depth profiles in the range of 5-10 μm could be obtained in 10-60 min. Calibration standards were prepared by ion implantation of a beam of 15 keV D_2 into polished (0.25 μm roughness) surfaces of 4037 and 1062 steel samples using the low energy mass separator at Chalk River Nuclear Laboratories. Ion doses of 1×10^{14} atoms/cm^2, 5×10^{14} atoms/cm^2 and 1×10^{15} atoms/cm^2 were implanted and the reference standards stored in liquid nitrogen until analysis.

RESULTS AND DISCUSSION

CONFIRMATION OF THE ELECTROCHEMICAL, THERMAL AND REDOX BEHAVIOUR OF R-1 THANOL

The assignment of the polarographic wave corresponding to the nitroxyl group of R-1 thanol was made unambiguously in Britton-Robinson buffers of pH 1.9 and 6.5 by comparison with the DC polarogram of a related compound, 2,2,6,6 tetramethyl oxypiperidine, which does not have the electroreducible carbonyl group at approximately -0.96 V vs. SCE.

The nitroxyl half-wave potential was located at +0.081 V at pH 1.9 and -0.065 V at pH 6.5 (versus SCE). The thermal stability of R-1 thanol was evaluated by means of differential pulse polarography. The degradation of a 10^{-4} M solution at 25°C in a Britton-Robinson buffer of pH 6.3 was found to follow first order kinetics with a half-life of 300 h. The reaction with atomic hydrogen is rapid, and its selectivity was confirmed by the observation that no reaction occurred when gaseous molecular hydrogen alone was passed through the solution.

To test the utility of R-1 thanol as a reagent suitable for the determination of atomic hydrogen, 100 mL of a 10^{-2} M solution in Britton-Robinson buffer of pH 1.88 was allowed to react with 1.7 mg of zinc dust. The extent of reaction was determined by analysing aliquots of the resulting solution by means of differential pulse polarography and electron spin resonance spectroscopy (Fig. 1). Polarographic analysis gave a value of 47.6% reacted while the ESR data indicated that 46.5% of the R-1 thanol had been consumed, both results in good agreement with the theoretical value of 52.0% for complete molar reaction of the reagents.

ANALYSIS OF STEEL SAMPLES

Samples of 4037 and 1062 steel were electrolysed in a solution of 0.4 M sodium sulphate containing 2×10^{-6} M R-1 thanol following the procedure of Klychako et al. (8). The pH of the analyte containing dissolved iron and unreacted R-1 thanol fell from 6.2 to about 5.2 with the dissolution of 0.5 to 0.20 g of steel. The consumption of R-1 thanol could not be determined directly by differential pulse polarography in this base electrolyte since its half-wave reduction potential is too close to the oxidation potential for mercury and the reduction potential of iron (III). Our efforts to reproduce the amperometric titration method described in the literature (8) were unsuccessful. The final concentrations of R-1 thanol were, however, measurable by ESR after precipitation and filtration of iron as hydroxide. These data are presented in Table 1 and Fig. 2.

The total hydrogen content of the steel samples was determined by the hot extraction method, and these data are also given in Table 1. There is good agreement between the hydrogen values obtained by the two techniques for the first two samples, but the hydrogen concentration values obtained by electrolysis/ESR were three to four times higher than the hot-extraction values

in the case of the last two samples. It is likely that hydrogen enrichment in the surface layers (9) is the reason for the high values observed after anodic dissolution and ESR analysis.

SIMS

On the basis of improved success in the bend test after exposure to NAP acid mixture, Rogers et al. (5) hypothesized that embrittlement originated in the surface layers of the metal. Secondary ion mass spectrometry provides a direct and convenient way of confirming this hypothesis because of its sensitivity in measuring concentration profiles. Profiles for deuterium-charged 1062 and 4037 steels, with and without NAP treatment are given in Fig. 3 and 4 and reveal surface enrichment in the first 10 μm of the steel.

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Table 1. Analysis of 4037 steel samples for hydrogen.

			Hydrogen (ppm)	
Sample No.	ESR peak height	% R1 rxn	ESR	Hot extraction
Reference	70.0	0		
S1	3.51	95.0	2.8	3.0
S2	12.0	82.9	6.0	7.3
S3	8.1	88.6	6.5	1.9
S4	13.2	81.4	4.0	0.9

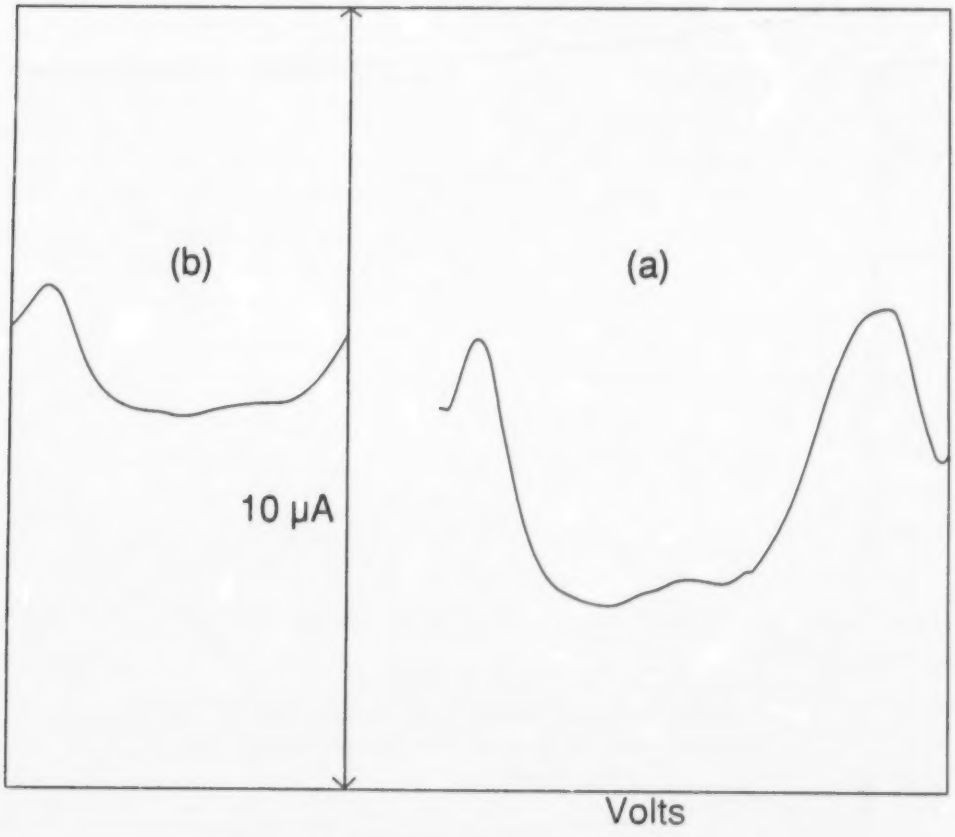

Fig. 1. Polarograms of R-1 Thanol before and after reaction with hydrogen.

Fig. 2. ESR Spectra of R-1 Thanol.

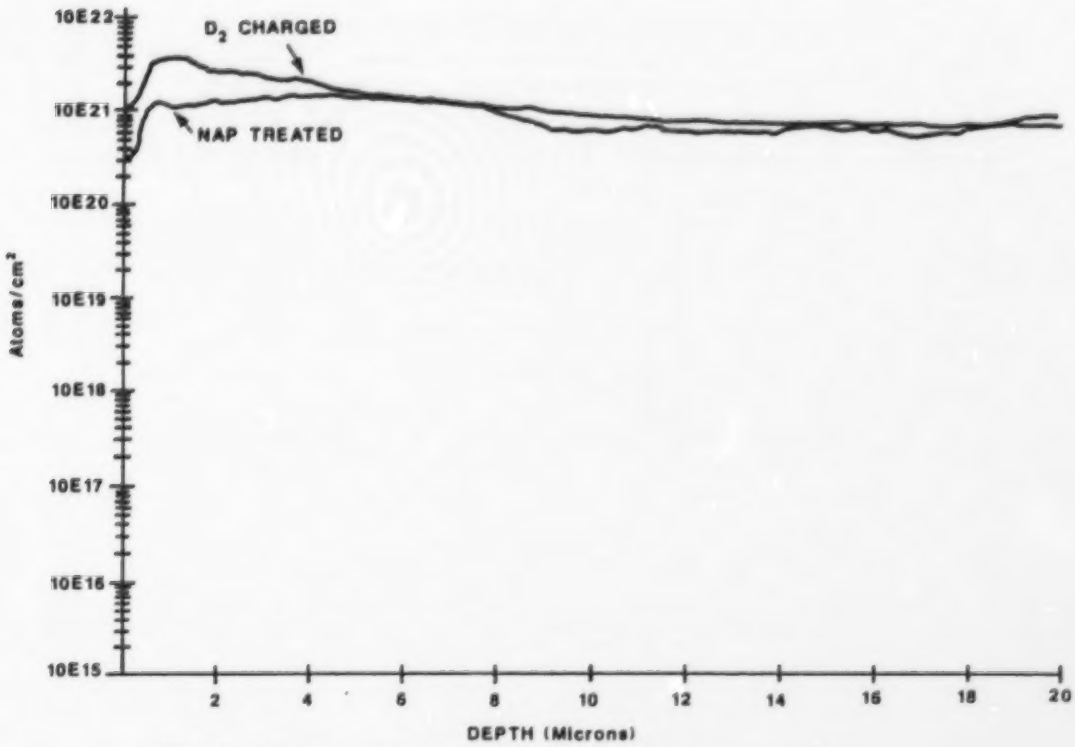

Fig. 3. Surface D_2 concentration vs depth profiles for 4037 steels with and without NAP solution treatment.

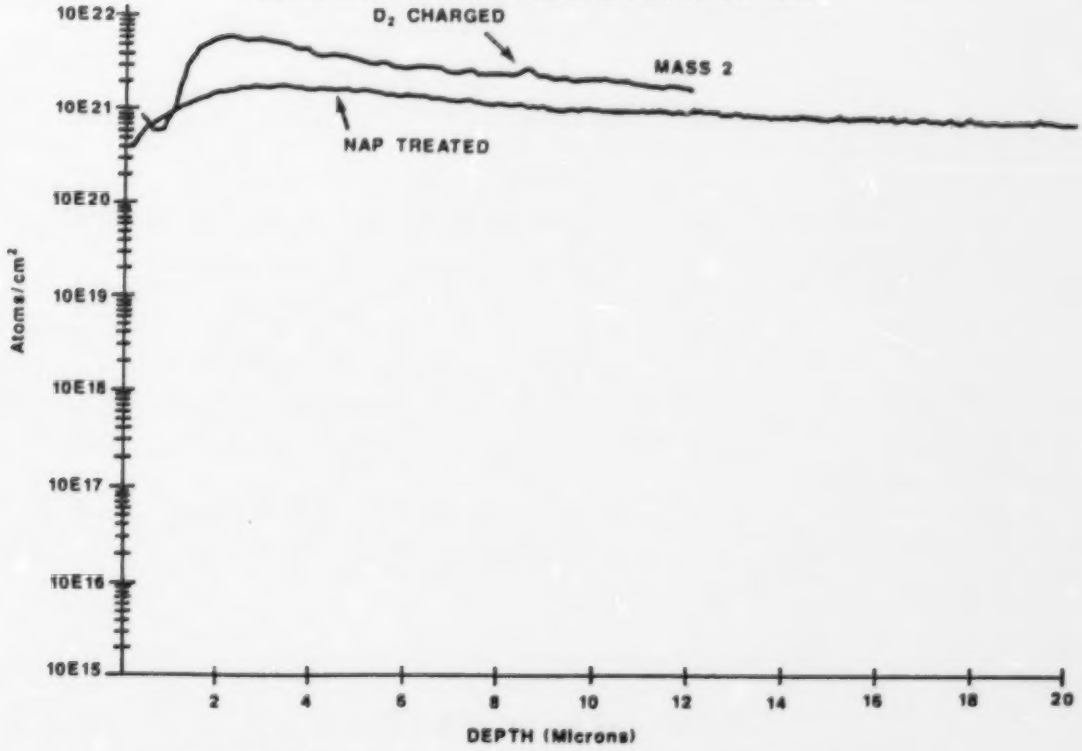

Fig. 4. Surface D_2 concentation vs depth (micron) profiles for 1062 steels with and without NAP solution treatment.